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BINDERS FOR FLUORSPAR PELLETS

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ABSTRACT

Fluorspar pellets produced in southern Illinois are used as a flux in the open-hearth and basic oxygen processes for manufacturing steel. Pellets are made from high quality flotation fluorspar with water glass used as a binder. The pellets are strong and ship well but tend to be dusty when handled in bulk.

The Illinois State Geological Survey experimented with binders and hardening temperatures to determine how dustiness might be eliminated. Binders studied included western bentonite and a southern Illinois clay, used by themselves and in combination with chemical fluxes. Hard, dustless pellets were produced with these binders at 1700° to 1900° F without addition of water glass.

When the experimental pellets were heated to these temperatures, fluorine gas evolved. The amount of fluorine depended on the temperature and on the binder used. The least evolution of fluorine took place when a binder of Illinois clay was treated with a small percentage of soda ash.

BINDERS FOR FLUORSPAR PELLETS

INTRODUCTION

Flotation fluorspar has been pelletized in a commercial plant in southern Illinois and sold largely to the steel industry since the summer of 1964. The pellets, which contain about 70 percent effective calcium fluoride (CaF_2), are three-eighths to one inch in diameter. They have sufficient strength to withstand the usual handling and shipping conditions encountered in their distribution and use. Uniform composition and size and ease in handling make them ideally suitable for basic oxygen furnaces where fluxing and other materials must be added quickly in specific amounts.

The pelletizing plant in southern Illinois uses finely ground fluorspar directly from the flotation cells in which lead and zinc sulfides and most of the associated rock minerals have been removed. This purified fluorspar, after partial drying, is fed to a rotating pelletizing disc 8 feet in diameter. Water glass and a small amount of bentonite are added for binder. The pellets formed on the disc are transferred onto a traveling belt and conveyed through an oil-fired oven where they are dried and heated to about 600° F. The emerging pellets are screened to remove those that are under- or over-sized. Although of variable strength, they can withstand an average compressive load of about 60 pounds.

Continuous operation of the pelletizing plant has shown that water glass, containing about 3.2 parts of SiO_2 to 1.0 part of Na_2O, is a satisfactory binder, especially when one-half to one percent of bentonite is added to improve the green strength of the pellets. Finished pellets, however, tend to be dusty when loaded into or out of a barge or truck, and, although the loss in material is negligible, this does present a minor problem. The Illinois State Geological Survey, consequently, has undertaken to determine how this dust might be eliminated by changing the binder and using a higher firing temperature.

EXPERIMENTAL PROGRAM

To determine the effect of various binders and firing temperatures, pellets were made in the laboratory by a uniform procedure involving hand molding and rolling in a rotating tire to simulate disc forming. A selected binder and enough water to allow proper balling were added to the finely ground fluorspar. Pellets were air dried for 60 minutes and tested for

green strength in a device that applied pressure slowly and consistently until the pellet cracked or broke open. At this point, the applied pressure was read and recorded.

Other pellets were similarly tested after heat drying at 300° F. The remaining pellets, after heat drying, were transferred directly into a muffle furnace preheated to a specific temperature. After being fired, usually for 20 to 30 minutes, they were removed from the furnace and allowed to air cool before they were tested for strength.

Binders

A practical binder for fluorspar pellets must be relatively inexpensive, with consideration given to the percentage required for strength. The binder also must either harden with the spar at a relatively low temperature, as does water glass, or it must cause the pellets to maintain their shape while being heated to a higher hardening temperature, which may be considered the temperature of incipient fusion. In such a case, the binder may influence this hardening temperature, and thus determine the temperature required to develop strength. Bentonite and certain clays are examples of this type of binder. The use of organic binders, such as starch or lignitic products, has not to our knowledge produced fluorspar pellets that are sufficiently weather resistant to be stored in the open.

Experiments with Water Glass

In a series of experiments, from 4 to 10 parts of water glass were used as a binder for each 100 parts of fluorspar. (Philadelphia Quartz Co. Type N, sp. gr. 11.6 pounds per gallon.) Three-quarters of a part of bentonite was added in each case to improve green strength. Results of experiments are shown in table 1.

These pellets containing water glass appear to develop full strength, or nearly so, when thoroughly dried. Additional heating to 1000° F does not increase strength appreciably. Although pellets become stronger as the percentage of water glass is increased, the higher percentages probably make complete drying more difficult so that a longer drying time or a higher temperature is required to develop full strength.

Experiments with Bentonite

A second series of experiments was made in which no water-glass binder was added, and Wyoming bentonite, either alone or in combination with certain fluxes, was used as binder. These pellets, after drying, were fired and tested for strength at 100° temperature intervals from 1500° to 1900° F. Results of these tests are shown in table 2.

Pellets containing only bentonite for binder develop a strength of 50 pounds or more in the temperature range between 1700° and 1800° F. At and above 1800° F, they have hard, vitreous surfaces that should eliminate

TABLE 1 - FLUORSPAR PELLETS MADE WITH WATER-GLASS BINDERS

Binder Ratio per 100 parts fluorspar	Pellet strength (lbs) Green	 Dried at 300° F	Pellet strength (lbs) at firing temperatures (F) 650°	 750°	 850°	 1000°
4 parts water glass 3/4 part bentonite	0.84	4.9	4.8	5.0	5.25	5.25
7 parts water glass 3/4 part bentonite	1.0	11.2	13.5	13.8	13.4	13.3
10 parts water glass 3/4 part bentonite	1.38	25.8	35.0	35.1	32.5	28.8

TABLE 2 - FLUORSPAR PELLETS MADE WITH BENTONITE BINDERS

Binder Ratio per 100 parts fluorspar	Pellet strength (lbs) Green	 Dried at 300° F	Pellet strength (lbs) at firing temperatures (F) 1500°	 1600°	 1700°	 1800°	 1900°
1 part bentonite	0.88	2.9	15	20	35	94	165
2 parts bentonite	0.68	5.9	15	23	29	67	180
1 part bentonite 1 part soda ash	0.53	2.0	13	18	27	64	179
1 part bentonite* 2 parts soda ash	0.58	2.9	52	48	71	54	101
1 part bentonite 1 part slaked lime	0.58	2.5	5	--	13	28	106
1 part bentonite 2 parts slaked lime	0.54	2.6	5	--	13	23	75

*These pellets cracked badly during drying and firing.

any dust problem. In addition, they have a near-white color and are attractive. In our experience, 1 part of bentonite per 100 parts of fluorspar is sufficient to give the desired strength. These pellets show no tendency to soften or stick together at firing temperatures up to 2000° F, the highest temperature tried.

An attempt was made to reduce the temperature at which strength was developed when using one part of bentonite by adding up to two parts of fluxing materials such as sodium chloride, soda ash, or slaked lime. The only additive causing appreciable reduction in the hardening temperature, however, was soda ash. When two parts of soda ash were added along with one part of bentonite, the pellets attained an average strength of 52 pounds at 1500°F. The pellets remained in this approximate strength range through 1800°F. This combination of binders is not practical, however, as these pellets cracked badly on drying and heating, and only a small percentage of them remained intact and could be tested for strength. This cracking probably accounted for the lower than expected strength determined at 1900° F. A second batch of pellets, which was made and tested with this combination of binders, showed the same results.

In another series of tests similar to the above, slaked lime was added with bentonite in place of soda ash. Results of these tests (table 2) indicate that the addition of lime was detrimental to pellet strength.

Pellets containing sodium chloride showed some indication of a lowered hardening temperature, but a layer of powdery material consistently formed on the surfaces during drying and remained there regardless of subsequent heating. Dust, therefore, was increased rather than eliminated. Results of these tests are not shown in the table.

Experiments with Illinois Clay

Following the experiments with bentonite, other pellets were tested in which a southern Illinois montmorillonitic clay was substituted for bentonite as the binding material. This clay is found in Pulaski County, Illinois, not far from the fluorspar mining area, and can be prepared in a size approximating that of the Wyoming bentonite presently used. Results of these tests are shown in table 3.

This Illinois clay, when used by itself as a binder, produced pellets with desirable green strength but low dry strength. The fired pellets were satisfactory when heated to 1800° F and higher, although their strength equaled that of the bentonite pellets only in the 1900° F range.

When this Illinois clay was chemically treated by adding one part of soda ash to each nine parts of clay (making the mixture 10 percent soda ash), and when 1 part of this mixture was used as binder per 100 parts of fluorspar, the dry strength of the fluorspar pellets was more than doubled and the fired strength exceeded that obtained with bentonite. Tests indicated that satisfactorily strong, dustless pellets could be produced throughout a temperature range of from 1700° to 1900° F. Tests also showed that these pellets had no tendency to soften or stick together when heated to 2000° F.

TABLE 3 - FLUORSPAR PELLETS MADE WITH ILLINOIS CLAY BINDERS

Binder	Pellet strength (lbs)		Pellet strength (lbs) at firing temperatures (F)				
Ratio per 100 parts fluorspar	Green	Dried at 300° F	1500°	1600°	1700°	1800°	1900°
1 part Illinois clay	0.79	1.0	6	15	22	55	174
2 parts Illinois clay	0.73	1.6	8	13	21	57	158
1 part Illinois clay (treated with 10 percent soda ash)	0.75	2.4	16	27	50	98	187
2 parts Illinois clay (treated with 10 percent soda ash)	0.85	3.2	7	12	21	52	200
1 part Illinois clay 1 part soda ash	0.65	3.6	13	17	26	66	175
1 part Illinois clay 2 parts soda ash	0.63	4.7	29	42	46	86	125
1 part Illinois clay 1 part slaked lime	0.70	3.8	7	16	28	59	192
1 part Illinois clay 2 parts slaked lime	0.65	4.5	6	16	23	54	155

TABLE 4 - FLUORINE EVOLUTION FROM PELLETS FIRED AT HARDENING TEMPERATURES OF 1500° to 1900° F

Binder	Fluorine evolution (ppm) at firing temperatures (20 minutes)				
Ratio per 100 parts fluorspar	1500° F	1600° F	1700° F	1800° F	1900° F
1 part bentonite	37	61	118	212	540
1 part bentonite 2 parts soda ash	65	69	59	105	256
1 part Illinois clay (treated with 10 percent soda ash)	21	13	74	67	72
1 part Illinois clay 2 parts soda ash	14	18	72	40	156

Other pellets in which Illinois clay and larger amounts of soda ash were used (1 and 2 parts per 100 parts of fluorspar) had no apparent advantage over those made with much less soda ash. In addition, the cost of binder was much higher. These pellets were very similar in strength to those made with bentonite and soda ash except that pellets containing one part of Illinois clay and two parts of soda ash did not crack when heated as did those containing bentonite.

Slaked lime was added to the Illinois clay as it was to bentonite. Here, however, one part of lime gave results similar to those obtained with an equal amount of soda ash, but there was no apparent advantage in increasing the amount of lime.

Binder Costs

Only approximate costs of binders can be discussed in this paper, as actual delivered costs of the various binder materials would vary for different locations. However, the values computed for binder costs per ton of pellets are thought to be sufficiently accurate to provide useful comparisons.

Assuming that water-glass solution at about 38 percent solids content (type N) costs $1.50 per 100 pounds, and bentonite in bags delivered in less-than-carload lots costs $40 per ton, the binder cost per ton of pellets using 5 percent water glass and 1 percent bentonite would then be about $1.85. An increase in water glass to obtain higher strength could easily boost the cost of binder to well over $2.00 per ton of pellets.

If, however, one part of bentonite were used as binder without water glass or other additive, the binder cost would drop to about 40 cents per ton of pellets. Assuming also that southern Illinois clay of the desired quality and preparation could be delivered to a southern Illinois pelletizing plant for $15.00 per ton, and that this clay would be treated by blending 10 percent soda ash at $40.00 per ton, the binder cost for using 1 percent of this mixture would be about 17.3 cents per ton of pellets.

The large difference in costs between clay and water glass plus bentonite would, of course, be offset partially by increased heating costs, assuming the all-bentonite or clay pellets had to be fired at about 1800° F, compared with about 600° F for the pellets made with water-glass binder.

Fluorine Evolution During Firing

In the present commercial method of pelletizing, with water glass as the primary binder and the pellets heated to a maximum temperature of about 600° F, there is no apparent evolution of fluorine or fluorine-containing gas that would cause corrosion of equipment or air pollution. A method employing bentonite or clay as the primary binder, which requires the pellets to be heated to 1700° F or higher, would change this situation. The fluorine that would be evolved might be diluted with air and discharged into the atmosphere, although scrubbing of the off-take gases from the heater by passing them through a bed of crushed limestone or other alkaline material might be required.

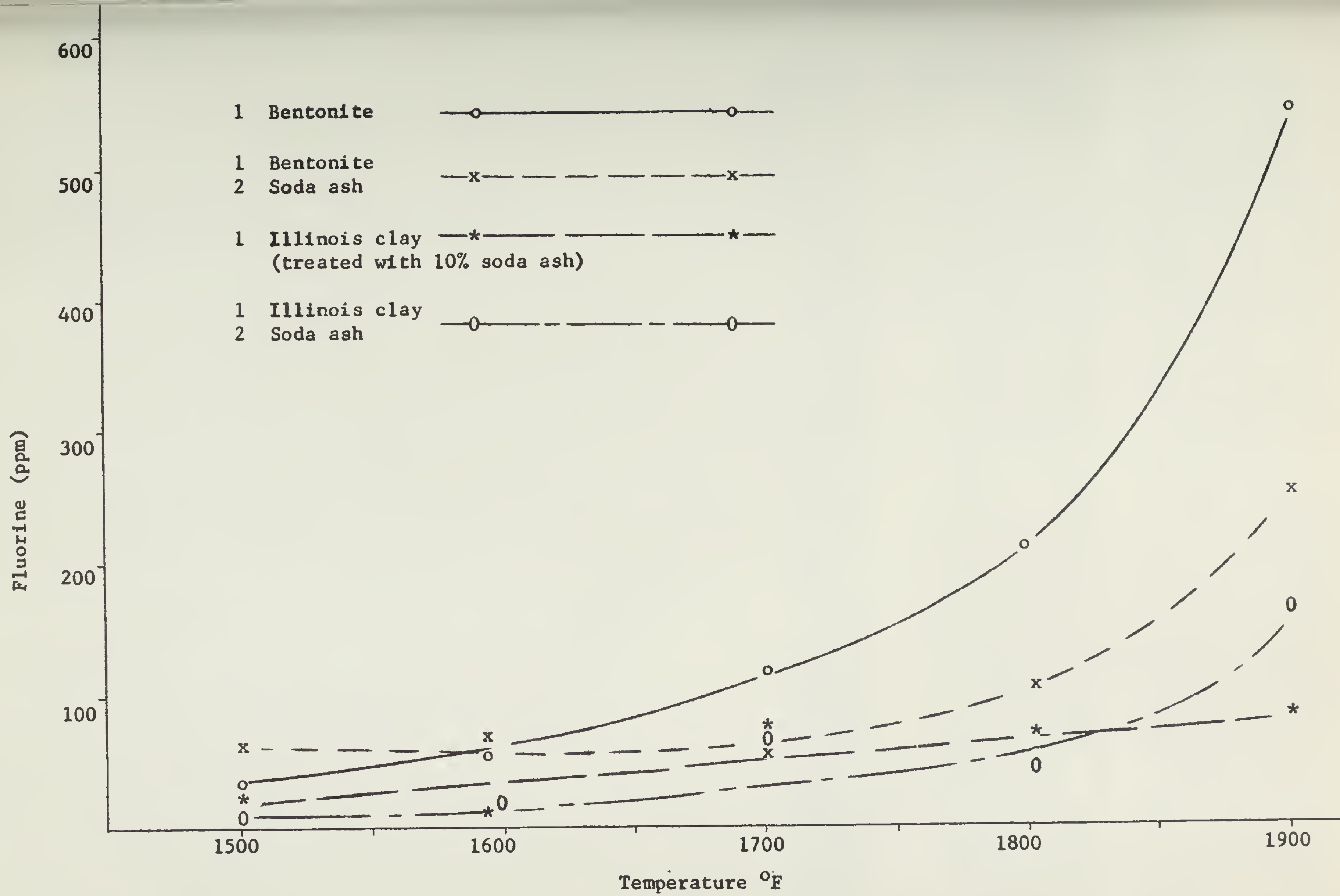

Fig. 1 - Fluorine evolution during heating

An effort has been made to determine the amount of fluorine that would be evolved and how this evolution would be affected by the binder used in the pellets. Table 4 shows the results of fluorine evolution tests made over a temperature range of 1500° to 1900° F on four series of pellets for which different binders had been used. Results are shown in parts per million (ppm) of fluorine evolved, based on the weight of the dry pellets. These data have been plotted in figure 1 to indicate more clearly the trends in fluorine evolution as the pellets are fired at the temperatures studied.

In these tests, the pellets dried at 300° F were heated in a combustion tube at the indicated temperature for 20 minutes. A stream of oxygen was passed over the pellets to flush out any evolved gases containing fluorine. These gases were absorbed in distilled water and the fluorine was determined by a modified acid-base titration. Duplicate tests, which were made on all pellets, checked well at temperatures up to and including 1800° F. There is some doubt about the accuracy of the values reported at 1900° F, as these duplicates checked less well. However, they are thought to be reasonably correct.

It is significant that much less fluorine was evolved when Illinois clay (plus 10 percent soda ash) was used for binder than when bentonite was used. It is also significant that the addition of soda ash to the bentonite binder reduced fluorine evolution approximately one-half at temperatures above 1600° F.